

# PATENT SPECIFICATION

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(19)



## (54) PROCESS FOR THE CONVERSION OF HYDROCARBONS

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the catalytic conversion of hydrocarbons in the presence of hydrogen and in particular to the preparation of high viscosity index lubricating oils by hydrocracking a mixture of heavy hydrocarbons. The invention also relates to hydrocarbons thus obtained.

In the preparation of high viscosity index lubricating oils by hydrocracking a mixture of heavy hydrocarbons, low viscosity index compounds present in the feed are converted into high viscosity index compounds. At the same time the nitrogen, sulphur and oxygen content of the oil is greatly reduced.

The suitability of catalysts for application in the preparation of high viscosity index lubricating oils by hydrocracking a mixture of heavy hydrocarbons depends on their temperature requirement, aromatic retention, and selectivity, which are defined as follows. Under given operating conditions and starting from a given feed for the preparation of a lubricating oil having a pre-determined viscosity index after dewaxing, the "temperature requirement" is the temperature which has to be used in order to obtain such a lubricating oil, the "aromatic retention" is the percentage of aromatics present in the said lubricating oil, based on the aromatic content of the feed, and the "selectivity" is the yield of the said lubricating oil. The lower the temperature requirement and the aromatic retention of the catalysts are and the higher the selectivity, the more suitable they are for the preparation of high viscosity index lubricating oils by hydrocracking a mixture of heavy hydrocarbons.

In the past, a great many catalysts have been proposed for the preparation of high

viscosity index lubricating oils by hydrocracking a mixture of heavy hydrocarbons. These catalysts generally contain one or more metals of groups VIB, VIIB and/or VIII or sulphides or oxides thereof supported on a carrier comprising one or more oxides of elements of Group II, III or IV. These catalysts may further comprise promoters such as phosphorus or boron and a halogen, such as chlorine or fluorine.

An extensive investigation carried out by applicant into the suitability of catalysts of the above-mentioned type for the preparation of high viscosity index lubricating oils by hydrocracking a mixture of heavy hydrocarbons has revealed that their suitability for this purpose is very highly dependent on the sort and quantity of metals and halogen present on the carrier and on the type of carrier and its properties.

A number of the investigated catalysts of the above-mentioned type proved to be totally unsuitable for the said application, because their temperature requirement and aromatic retention were far too high, while their selectivity was far too low. Most of the investigated catalysts were moderately suitable for the said application. However, either the temperature requirement or the aromatic retention or the selectivity of these catalysts was inadequate for optimum catalyst performance. A small group of catalysts of the above-mentioned type, however, displayed an excellent performance in the preparation of high viscosity index lubricating oils by hydrocracking a mixture of heavy hydrocarbons. The temperature requirement and aromatic retention of these catalysts was very low, while their selectivity was very high. Further investigation regarding catalysts of the above-mentioned type for the preparation of high viscosity index lubricating oils by hydrocracking a mixture of heavy hydrocarbons revealed that in order to obtain the best performance these catalysts must meet the following requirements.

The finished catalyst should have a compacted bulk density of at least 0.8 g/ml, and should comprise at least 3 parts by weight

of nickel and at least 20 parts by weight of tungsten per 100 parts by weight of alumina carrier, in addition to fluorine. By compacted bulk density of a material is meant in this patent application the quotient of the weight of a given quantity of the material and the volume thereof after thorough compaction, which may very suitably be effected by means of an electric vibrator.

The catalyst should be prepared from an alumina hydrogel. This alumina hydrogel should possess the property that a xerogel can be obtained therefrom by drying and calcining, which xerogel has a compacted bulk density of less than 0.8 g/ml. The route via which the catalyst is prepared from this hydrogel depends on the pore volume quotient of the said xerogel. By the pore volume quotient of a substance is meant in this patent application the quotient of the mercury pore volume and the total pore volume of the substance, the mercury pore volume being defined as the pore volume present in pores having a diameter larger than 7.5 nm determined with mercury and the total pore volume being defined as the sum of the pore volume present in pores with a diameter small than 60 nm determined with nitrogen and the pore volume present in pores with a diameter of at least 60 nm determined with mercury. If the pore volume quotient of the said xerogel is at least 0.5, the preparation of the catalyst may in principle be effected in two ways, which may be designated as the hydrogel route and the xerogel route; if the pore volume quotient of the said xerogel is less than 0.5, only one of the two ways, namely the hydrogel route, is suitable for the preparation of the catalyst.

The preparation of the catalysts via the xerogel route from an alumina hydrogel from which a xerogel can be obtained by drying and calcining, which xerogel has a compacted bulk density of less than 0.8 g/ml and a pore volume quotient of at least 0.5, is effected by drying and calcining the alumina hydrogel, incorporation of the metals and optionally fluorine into the xerogel, and drying and calcining the composition.

The preparation of the catalysts via the hydrogel route from an alumina hydrogel from which a xerogel can be obtained by drying and calcining, which xerogel has a compacted bulk density of less than 0.8 g/ml and a pore volume quotient of at least 0.5, is effected by incorporation of the metals and optionally fluorine into the alumina hydrogel, and drying and calcining the composition.

The preparation of the catalysts via the hydrogel route from an alumina hydrogel from which a xerogel can be obtained by drying and calcining, which xerogel has a compacted bulk density of less than 0.8 g/ml and a pore volume quotient of less than 0.5, is effected by incorporation of the metals and at least

part of the fluorine into the alumina hydrogel, and drying and calcining the composition; in this preparation of the catalyst, such an amount of fluorine should be incorporated in the alumina hydrogel that a xerogel with a pore volume quotient of at least 0.5 can be obtained, by drying and calcining, from the same alumina hydrogel when the same amount of fluorine, but no metals are incorporated therein.

In addition to their application as catalyst for the preparation of high viscosity index lubricating oils by hydrocracking a mixture of heavy hydrocarbons, the catalysts according to the invention are also suitable for application in other processes in which hydrocarbons are converted at elevated temperature and pressure and in the presence of hydrogen.

The present invention provides a process for the conversion of hydrocarbons in which the hydrocarbons are contacted at elevated temperature and pressure and in the presence of hydrogen with a fluorine-containing nickel-tungsten catalyst having an alumina as carrier, which catalyst has a compacted bulk density of at least 0.8 g/ml, comprises at least 3 parts by weight of nickel and at least 20 parts by weight of tungsten per 100 parts by weight of carrier, and is prepared as follows from an alumina hydrogel from which a xerogel having a compacted bulk density of less than 0.8 g/ml can be obtained by drying said hydrogel at 120°C. and calcining at 550°C.:

- 1) If the pore volume quotient of the said xerogel is at least 0.5, the preparation of the catalyst is effected either
  - a) by drying and calcining the alumina hydrogel, incorporation of the metals and optionally fluorine into the xerogel, and drying and calcining the composition, or
  - b) by incorporation of the metals and optionally fluorine into the alumina hydrogel, and drying and calcining the composition.
- 2) If the pore volume quotient of the said xerogel is less than 0.5, the preparation of the catalyst is effected by incorporation of the metals and at least part of the fluorine into the alumina hydrogel, and drying and calcining the composition, with the proviso that such a quantity of fluorine is incorporated that a xerogel with a pore volume quotient of at least 0.5 can be obtained, by drying at 120°C and calcining at 550°C, from the same alumina hydrogel when the same quantity of fluorine, but no metals, are incorporated therein.

Only certain alumina hydrogels are suitable for the preparation of catalysts applicable according to the present invention. In order to determine whether an alumina hydrogel is

suitable to serve as starting material for the preparation of the catalyst and, if so, to determine further via which route the preparation of the catalyst can be effected, a sample of the hydrogel concerned is dried at 120°C and calcined at 550°C. The compacted bulk density and the pore volume quotient of the resultant xerogel are determined. Only if the compacted bulk density of the said xerogel is less than 0.8 g/ml is the hydrogel suitable to be applied as starting material in the preparation of catalyst. The pore volume quotient of the said xerogel determines via which route the preparation of the catalyst should be carried out. If the pore volume quotient of the said xerogel is at least 0.5, both the xerogel route and the hydrogel route are suitable; if the pore volume quotient is less than 0.5, only the hydrogel route is suitable, while it should also be ensured that during the preparation of the catalyst via the hydrogel route, sufficient fluorine is incorporated in the hydrogel. The minimum quantity of fluorine which should be incorporated in the hydrogel during the preparation of the catalyst can be determined by incorporating different quantities of fluorine in a number of samples of the hydrogel concerned and drying the fluorine-containing hydrogels at 120°C and calcining them at 550°C. The pore volume quotient of the resultant fluorine-containing xerogels is then determined. The above-mentioned minimum quantity of fluorine is that which yields a fluorine-containing xerogel with a pore volume quotient of 0.5.

If the xerogel route is used for the preparation of the present catalyst, the alumina hydrogel is first dried and calcined, subsequently the metals and optionally fluorine are incorporated into the calcined material and finally the composition is dried and calcined. The incorporation of the metal into the calcined material may be very suitably effected by impregnating the said material with an aqueous solution comprising a nickel compound and a tungsten compound. Fluorine may be incorporated in the catalyst either by impregnation or by in-situ fluoriding. If fluorine is incorporated into the catalyst by impregnation this may be done either together with nickel and tungsten, or in a separate impregnation step with an aqueous solution of a fluorine compound. Incorporation of fluorine into the catalyst by impregnation is preferably performed in a separate impregnation step which is carried out after nickel and tungsten have been incorporated into the calcined material and the latter has been recalcined. In-situ fluoriding of the catalyst can be effected by supplying, during the initial phase of the process for which the catalyst is used, a given quantity of a fluorine compound to the gas and/or liquid stream which is passed over the catalyst until the required fluorine content of the catalyst has been reached. If in the process

according to the invention use is made of a catalyst prepared via the xerogel route, a catalyst is preferably employed into which at least some of the fluorine, and preferably substantially all of the fluorine, has been incorporated by in-situ fluoriding.

If the hydrogel route is used for the preparation of the present catalysts, the metals and optionally fluorine are incorporated into the hydrogel and subsequently the composition is dried and calcined. The incorporation of the metals into the hydrogel may very suitably be effected by treating them with an aqueous solution comprising a nickel compound and a tungsten compound. This treatment is carried out preferably at a temperature above 50°C and in particular at a temperature between 60 and 250°C. Fluorine may be incorporated into the catalysts either while the alumina is still in the hydrogel form or after calcining of the composition, or by in-situ fluoriding. Incorporation of fluorine into the catalyst while the alumina is still in the hydrogel form is preferably effected by treating the hydrogel with an aqueous solution comprising a nickel compound, a tungsten compound and a fluorine compound. If for the process according to the invention use is made of a catalyst prepared via the hydrogel route, a catalyst is preferably employed into which at least some of the fluorine and more particularly substantially all the fluorine is incorporated while the alumina is still in the hydrogel form.

Catalysts which are suitable to be employed in the process according to the invention comprise at least 3 parts by weight of nickel and at least 20 parts by weight of tungsten per 100 parts by weight of alumina.

If the catalysts are prepared via the xerogel route, preference is given to catalysts comprising 3—12 parts by weight of nickel and 20—75 parts by weight of tungsten per 100 parts by weight of alumina and in particular to catalysts in which furthermore the nickel to tungsten weight ratio is between 1:5 and 1:7. The catalysts prepared via the xerogel route preferably comprise 0.5—20 parts by weight of fluorine per 100 parts by weight of alumina, with the proviso that if these catalysts are used for the preparation of high viscosity index lubricating oils by hydrocracking a mixture of heavy hydrocarbons, their fluorine content should preferably be 0.5—10 parts by weight per 100 parts by weight of alumina, while if they are used for the preparation of light hydrocarbons by hydrocracking a mixture of heavy hydrocarbons, their fluorine content should preferably be 10—20 parts by weight per 100 parts by weight of alumina.

If the catalysts are prepared via the hydrogel route, preference is given to catalysts comprising 25—50 parts by weight of nickel and 50—80 parts by weight of tungsten per 100 parts by weight of alumina and in particular

to catalysts in which furthermore the nickel to tungsten weight ratio is between 1:1.5 and 1:5. The catalysts prepared via the hydrogel route preferably comprise 10—30 parts by weight of fluorine per 100 parts by weight of alumina, with the proviso that if these catalysts are used for the preparation of high viscosity index lubricating oils by hydrocracking a mixture of heavy hydrocarbons, their fluorine content should preferably be 10—25 parts by weight per 100 parts by weight of alumina, while if they are employed for the preparation of light hydrocarbons by hydrocracking heavy hydrocarbons, their fluorine content should preferably be 20—30 parts by weight per 100 parts by weight of alumina.

Whereas the alumina hydrogels employed as starting material for the preparation of the catalysts have the characteristic feature that a xerogel with a compacted bulk density of less than 0.8 g/ml can be obtained therefrom by drying and calcining, the catalysts prepared on the basis of these hydrogels should have a compacted bulk density of at least 0.8 g/ml. Consequently an increase of the compacted bulk density should be brought about during the preparation of the catalyst. An increase of the compacted bulk density occurs inter alia on incorporation of the metals, the increase of the compacted bulk density becoming larger as a higher metal load is employed. An increase of the compacted bulk density may further be brought about by exerting pressure on the hydrogel, for example by kneading, pressing or extruding, the increase of the compacted bulk density becoming larger as the pressure exerted becomes higher. Pressing the hydrogel under high pressure through a narrow opening such as a slit produces a considerable increase of the compacted bulk density. The compacted bulk density — increasing effect of exerting pressure on the hydrogel may be appreciably amplified still further by incorporating certain additives into the hydrogel such as nitric acid and aluminium salts.

In addition to fluorine, the present catalysts may also comprise other promoters such as phosphorous and boron.

The metals nickel and tungsten may be present as such in the present catalysts or in the form of their oxides or sulphides. The catalysts are preferably employed in sulphidic form. Sulphiding of the present catalysts may be carried out according to any process known in the art for the sulphiding of catalysts. Sulphiding may for example be effected by contacting the catalysts with a sulphur-containing gas such as a mixture of hydrogen and hydrogen sulphide. Sulphiding may also be suitably carried out by contacting the catalyst with a sulphur-containing hydrocarbon oil such as a sulphur-containing gas oil.

The present catalysts are of particular importance for use in the preparation of high viscosity index lubricating oils by hydrocrack-

ing a mixture of heavy hydrocarbons. Preferred mixtures of heavy hydrocarbons which may serve as starting material for the preparation of lubricating oils according to the invention are waxy lubricating oil fractions obtained by distillation at reduced pressure of atmospheric distillation residues of waxy crude oils and waxes obtained from these waxy lubricating oil fractions or from waxy lubricating oil fractions prepared by hydrocracking. Examples of such waxy lubricating oil fractions are spindle oil (SO), light machine oil (LMO), and medium machine oil (MMO) waxy distillates and de-asphalted oils (DAO), SO, LMO and MMO waxy raffinates and waxy bright stocks (BS) obtained from the above-mentioned lubricating oil fractions by treating the latter with a selective solvent for aromatics such as furfural, and SO, LMO, MMO, DAO and BS slack waxes obtained from the above-mentioned lubricating oils by de-waxing. Mixtures of one or more distillate lubricating oil fractions and/or one or more residual lubricating oil fractions and/or one or more slack waxes may also be used as starting material for the preparation of lubricating oil according to the invention.

Hydrocracking a mixture of heavy hydrocarbons for the preparation of high viscosity index lubricating oils according to the invention is effected by contacting the mixture of heavy hydrocarbons at elevated temperature and pressure and in the presence of hydrogen with the catalyst, which is preferably present in one or more beds of particles having a diameter between 0.5 and 3 mm.

Suitable hydrocracking conditions are: a temperature from 325 to 450°C, a pressure from 10 to 250 bar, a hydrogen/feed ratio from 100 to 5000 N1 of hydrogen per kg of feed and a space velocity from 0.2 to 5.0 kg of feed per litre of catalyst per hour. It is preferable to employ the following conditions: a temperature from 350 to 425°C, a pressure from 100 to 200 bar, a hydrogen/feed ratio from 500 to 2500 N1 of hydrogen per kg of feed and a space velocity from 0.5 to 1.5 kg of feed per litre of catalyst per hour.

Lubricating oils prepared according to the invention have a low aromatic content. Lubricating oils with an even lower aromatic content can be prepared according to the invention if the hydrocracking step is followed by a hydrofinishing step. Hydrofinishing of the hydrocracked product can be effected by contacting the hydrocracked product at elevated temperature and pressure and in the presence of hydrogen with a hydrofinishing catalyst. The pressure, space velocity and gas velocity employed in the hydrofinishing step may be chosen within the same limits as defined above for the hydrocracking step. The hydrofinishing temperature is preferably selected between 225 and 400°C and in particular between 275 and

375°C. The temperature employed in the hydrofinishing step should be at least 25°C lower than the temperature at which the hydrocracking step is carried out. Suitable hydrofinishing catalysts are catalysts comprising one or more metals of Group VIB, VIIB or VIII of the Periodic Table on a carrier. The Periodic Table referred to herein may be found in "The Handbook of Chemistry and Physics", 39th Edition, Chemical Rubber Publishing Company (1957—1958).

The effluent from the hydrocracking reactor or, if hydrofinishing is employed, the effluent from the hydrofinishing reactor, is cooled and separated in hydrogen-rich gas and a liquid product. The liquid product comprises hydrocarbons which boil below the boiling range of lubricating oil and hydrocarbons which boil within this range. The hydrocarbons which boil below the said range are separated from the higher-boiling residue, preferably by fractional distillation. The cutting-point of this distillation is preferably so chosen that the higher-boiling residue has an initial boiling point in the range of 350 to 550°C. In addition to excellent lubricating oil components this residue generally comprises n-paraffins which solidify at ambient temperature and therefore impair the pour point of the lubricating oil. In order to obtain a suitable lubricating oil from the residue it is therefore preferred to de-wax this residue. The de-waxing treatment may be effected in any desired manner. De-waxing is preferably effected with a mixture of methyl-ethyl-ketone and toluene at a temperature between -10 and -40°C and at a solvent/oil volume ratio between 1:1 and 10:1. In order to raise the yield of lubricating oil it is preferred to recycle at least some of the separated paraffins to the hydrocracking reactor.

In addition to their application as catalyst in the hydrocracking of a mixture of heavy hydrocarbons for the preparation of high viscosity index lubricating oils, the present catalysts are also very suitable to be applied in the first stage of a two-stage process for the preparation of light hydrocarbons such as gasolines and kerosines by hydrocracking a mixture of heavy hydrocarbons such as gas oils, flash distillates and mixtures of flash distillates and de-asphalted oils. Examples of other processes according to the invention in which the present catalysts may be successfully applied are: the preparation of light hydrocarbons from a mixture of heavy hydrocarbons by single-stage hydrocracking, the hydrogenation of aromatics present in light fuels such as kerosines in order to improve the smoke point, the hydrodesulphurization of distillate and residual hydrocarbon fractions, the hydrofinishing of lubricating oils and the preparation of technical white oils and medicinal oils by catalytic hydrogen treatment of aromatic-poor mineral oil fractions.

The invention will now be elucidated with reference to the following examples.

A total of 37 catalysts were tested for the conversion of hydrocarbon oils at elevated temperature and pressure and in the presence of hydrogen. Of these 37 catalysts, 19 were within the scope of the invention (catalysts 1—19) and the other 18 were outside the scope of the invention (catalysts A—T). The preparation of the catalysts was carried out as follows.

#### CATALYSTS 1—13.

These catalysts were prepared via the xerogel route from an alumina hydrogel from which a xerogel could be obtained by drying and calcining, which xerogel had a compacted bulk density of 0.35 g/ml and a pore volume quotient of 0.8 (alumina hydrogel I).

The preparation of the catalysts 1—7 was effected by drying, extruding and calcining alumina hydrogel I, impregnating the extrudates with an aqueous solution comprising a nickel and a tungsten compound, and drying and calcining the impregnated extrudates.

The preparation of catalyst 8 was effected by drying, extruding and calcining alumina hydrogel I, impregnating the extrudates with an aqueous solution comprising a nickel compound, a tungsten compound, and a boron compound, and drying and calcining the impregnated extrudates.

Fluorine was incorporated into the catalysts 1—8 by in-situ fluoriding.

The preparation of the catalysts 9—13 was effected by drying, extruding and calcining alumina hydrogel I, impregnating the extrudates with an aqueous solution comprising a nickel compound and a tungsten compound, drying and calcining the impregnated extrudates, impregnating the calcined extrudates with an aqueous solution comprising a fluorine compound, and drying and calcining the impregnated extrudates. An additional quantity of fluorine was incorporated into the catalysts 10—13 by in-situ fluoriding.

#### CATALYSTS 14—19.

These catalysts were prepared via the hydrogel route. The catalysts 14—17 were prepared from the above-mentioned alumina hydrogel I. The catalysts 18 and 19 were prepared from an alumina hydrogel from which a xerogel could be obtained by drying and calcining, which xerogel had a compacted bulk density of 0.7 g/ml and a pore volume quotient of 0.3 (alumina hydrogel II).

The preparation of catalyst 14 was effected by mixing an aqueous solution comprising a nickel and a tungsten compound with alumina hydrogel I, and maintaining the mixture for some time at elevated temperature, separating from the mixture the hydrogel loaded with metals and subsequently drying, extruding and calcining the said hydrogel. Fluorine was

incorporated into catalyst 14 by in-situ fluoriding.

The preparation of the catalysts 15—19 was effected by mixing an aqueous solution comprising a nickel compound, a tungsten compound and a fluorine compound with either alumina hydrogel I (for the preparation of the catalysts 15—17) or alumina hydrogel II (for the preparation of the catalysts 18 and 19), and maintaining the mixture for some time at an elevated temperature, separating from the mixture the hydrogel loaded with metals and fluorine, and subsequently drying, extruding and calcining the said hydrogel. An additional quantity of fluorine was incorporated into the catalysts 16, 17 and 19 by in-situ fluoriding.

#### CATALYSTS A—E.

These catalysts were prepared via the xerogel route from the above-mentioned alumina hydrogels I and II.

The preparation of the catalysts A and B was effected by drying, extruding and calcining either alumina hydrogel I (for the preparation of catalyst A) or alumina hydrogel II (for the preparation of catalyst B), impregnating the extrudates with an aqueous solution comprising a nickel compound and/or tungsten compound, and drying and calcining the impregnated extrudates. Fluorine was incorporated into the catalysts A and B by in-situ fluoriding.

The preparation of the catalysts C—E was effected by drying, extruding and calcining alumina hydrogel II, impregnating the extrudates with an aqueous solution comprising a nickel compound and a tungsten compound, drying and calcining the impregnated extrudates, impregnating the calcined extrudates with an aqueous solution comprising a fluorine compound, and drying and calcining the impregnated extrudates. An additional quantity of fluorine was incorporated into the catalysts D and E by in-situ fluoriding.

#### CATALYSTS F AND G.

These catalysts were prepared via the hydrogel route from the above-mentioned alumina hydrogel II.

The preparation of catalyst F was effected by mixing an aqueous solution comprising a nickel compound and a tungsten compound with alumina hydrogel II and maintaining the mixture for some time at an elevated temperature, separating from the mixture the hydrogel loaded with metals and subsequently drying, extruding and calcining the said hydrogel. Fluorine was incorporated into catalyst F by in-situ fluoriding.

The preparation of catalyst G was effected by mixing an aqueous solution comprising a nickel compound, a tungsten compound and a fluorine compound with alumina hydrogel II and maintaining the mixture for some time at elevated temperature, separating from the mixture the hydrogel loaded with metals and fluorine, and subsequently drying, extruding and calcining the said hydrogel. An additional quantity of fluorine was incorporated into catalyst G by in-situ fluoriding.

#### CATALYSTS H—T.

These catalysts were prepared by impregnation of calcined carriers with an aqueous solution comprising one or two metal compounds and optionally a boron or a phosphorus compound, followed by drying and calcining of the compositions.

The preparation of catalyst H was effected by impregnation of a silica-zirconia carrier with an aqueous solution comprising a platinum compound, followed by drying and calcining of the composition.

The preparation of the catalysts J—M was effected by impregnation of an alumina carrier with an aqueous solution comprising a nickel compound, a molybdenum compound and a phosphorous compound, followed by drying and calcining of the composition. Fluorine was incorporated into the catalysts K—M by in-situ fluoriding.

The preparation of catalyst N was effected by impregnation of an alumina carrier with an aqueous solution comprising a nickel compound, a tungsten compound and a boron compound, followed by drying and calcining of the composition.

The preparation of the catalysts P—R was effected by impregnation of either an alumina carrier (for the preparation of catalyst P), or of a silica-alumina carrier (for the preparation of catalyst Q), or of a silica-magnesia carrier (for the preparation of catalyst R), with an aqueous solution comprising a nickel compound and a tungsten compound, followed by drying and calcining of the compositions.

The preparation of the catalysts S and T was effected by impregnation of a fluorine-containing alumina carrier with an aqueous solution comprising a nickel compound and either a tungsten compound (for the preparation of catalyst S) or a molybdenum compound (for the preparation of catalyst T), followed by drying and calcining of the compositions.

The chemical constitution of and some further data on the various catalysts is stated in the tables A and B.

TABLE A

Cat. No.	catalyst constitution in pbw per 100 pbw of alumina carrier			Route employed in the preparation of the catalyst		Alumina hydrogel employed for the preparation of the catalyst		Percentage of the quantity of the flourine present on the catalyst, applied by in situ fluorination	Compacted bulk density of the catalyst, g/ml
	Ni	W	F	Xerogel	Hydrogel	I	II		
1	5	30	6	+		+		100	0.9
2	5	30	15	+		+		100	0.9
3	5	30	10	+		+		100	0.9
4	7.5	45	15	+		+		100	0.9
5	10	60	15	+		+		100	1.0
6	10	30	15	+		+		100	0.9
7	3.5	30	15	+		+		100	0.9
8(*)	7.9	35.8	1	+		+		100	0.9
9	5	30	6	+		+		0	0.9
10	5	30	6	+		+		25	0.9
11	5	30	6	+		+		75	0.9
12	10	60	15	+		+		80	1.0
13	10	60	15	+		+		60	1.0
14	37	70	14		+	+		100	1.5
15	37	70	14		+	+		0	1.2
16	37	70	14		+	+		25	1.2
17	37	70	14		+	+		75	1.3

TABLE A (Continued)

Cat. No.	catalyst constitution in pbw per 100 pbw of alumina carrier		Route employed in the preparation of the catalyst		Alumina hydrogel employed for the preparation of the catalyst		Percentage of the quantity of the fluorine present on the catalyst, applied by in situ fluorination	Compacted bulk, density of the catalyst, g/ml
	Ni	W	F	Xerogel	Hydrogel	I	II	
18(**)	37	70	14		+		+	1.4
19(**)	37	70	14		+		+	1.5
A	2.5	15	15	+		+		0.7
B	5	30	6	+			+	1.2
C	5	30	6	+			+	1.2
D	5	30	6	+			+	1.2
E	5	30	6	+			+	1.2
F	37	70	14		+		+	1.9
G(**)	37	70	14		+		+	1.6

(\*) Catalyst 8 comprised additionally 4 pbw of boron per 100 pbw of alumina carrier.

(\*\*) In the hydrogels from which the catalysts 18, 19 and G were prepared, the amount of fluorine incorporated was such that the pore volume quotient of the xerogels which could be prepared from these fluorine-containing hydrogels by drying and calcining was 0.7, 0.6 and 0.4 respectively.



TABLE B

Catalyst constitution in parts by weight per 100 parts  
by weight of carrier

Cat. No.	Ni	Mo	W	Pt	P	B	F	Cat. carrier
H				0.6				SiO <sub>2</sub> ZrO <sub>2</sub>
J	3.0	10.5			1.8			Al <sub>2</sub> O <sub>3</sub>
K	3.8	16.0			4		3	Al <sub>2</sub> O <sub>3</sub>
L	2.7	15.6			2		2.5	Al <sub>2</sub> O <sub>3</sub>
M	10	20			2		2	Al <sub>2</sub> O <sub>3</sub>
N	7.9		35.8			4		Al <sub>2</sub> O <sub>3</sub>
P	4.9		26.3					Al <sub>2</sub> O <sub>3</sub>
Q	2.3		11.0					SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>
R	3.5		11.0					SiO <sub>2</sub> -MgO
S	2.3		11.0				2.5	Al <sub>2</sub> O <sub>3</sub>
T	2.3		14.4				2.5	Al <sub>2</sub> O <sub>3</sub>

## EXAMPLE I.

The temperature requirement, aromatic retention and selectivity of a number of the catalysts shown in Table A for the preparation of a 400°C<sup>+</sup> lubricating oil with a VI of 130 after de-waxing at -30°C, were intercompared in a hydrocracking test which was carried out under the following conditions.

## 10 Feed:

Oil obtained by de-asphalting a residue originating from the distillation under reduced pressure of an atmospheric distillation residue of a Middle East crude oil.

## 15 Properties of the feed:

VI after de-waxing at -30°C: 77  
sulphur content: 2.1 percent by weight  
nitrogen content: 630 pbwm  
aromatic content: 135 mmol/100 g

## 20 Hydrocracking conditions:

pressure: 150 bar  
space velocity: 1 1.1<sup>-1</sup>.hour<sup>-1</sup>

hydrogen/feed ratio: 2000 N1.1<sup>-1</sup>.

The catalysts were employed in sulphided form. Sulphiding of the catalysts was carried out by contacting them for 5 hours with a mixture of hydrogen and hydrogen sulphide in a volume ratio of 7:1 at a temperature between 75 and 275°C and a pressure of 10 bar. De-waxing was effected using a mixture of methyl-ethyl-ketone and toluene in a ratio of 1:1. In-situ fluoriding of the appropriate catalysts was effected by supplying 300 ppmw of fluorine in the form of ortho-fluoro-toluene to the feed during the initial phase of the test until the required fluorine content of the catalyst had been reached. The catalysts were tested in the form of 1.5 mm extrudates.

In this test, an optimum catalyst should have a temperature requirement of at most 420°C, an aromatic retention of at most 30%, and a selectivity of at least 35% by weight.

The results of this test are shown in table C.

TABLE C

No. of cat. tested	temperature requirement, °C	selectivity, % by weight of feed	aromatic retention, %
9	418	35	15
10	416	35	12
11	414	35	9
1	412	35	8
15	403	39	7
16	408	38	7.5
17	414	36	9
14	418	36	15
C	431	32	31
D	429	33	26
E	422	33	19
B	420	33	17
18	403	39	7
19	411	36	8
G	413	30	11
F	413	29	11

## EXAMPLE II.

5 The temperature requirement, aromatic re-  
 10 tention and selectivity of a number of the  
 catalysts shown in tables A and B for the  
 preparation of a 375°C+ lubricating oil with  
 a VI of 128 after de-waxing at -20°C, were  
 intercompared in a hydrocracking test which  
 was carried out under the same conditions as  
 the test described in example I.

## Feed:

15 oil obtained by de-asphalting a residue  
 originating from distillation at reduced pres-  
 sure of an atmospheric distillation residue  
 of a Middle East crude oil.

## Properties of the feed:

VI after de-waxing at -20°C: 81  
 sulphur content: 2.5% by weight  
 nitrogen content: 780 pbwm  
 aromatic content: 100 mmol/100 g 20

Catalyst bed: 100 ml

The catalysts were tested in the form par-  
 ticles with a diameter of from 0.5—1.4 mm.

In this test, an optimum catalyst should  
 have a temperature requirement of at most 25  
 420°C, an aromatic retention of at most 30%,  
 and a selectivity of at least 40% by weight.

The results of this test are shown in table D.

TABLE D

No. of cat. tested	Temperature requirement, °C	Selectivity, % by weight of feed	Aromatic retention, %
1	410	44	22
15	400	48	15
H(*)	440	36	80
J	433	38	47
P	435	38	53
Q	421	40	40
R	413	38	24
S	426	43	35
T	424	43	35

(\*) Under the conditions of this test it was not possible to prepare a lubricating oil with a VI of 128 using catalyst H. The figures for catalyst H shown in table D relate to the preparation of an oil with a VI of 112.

### EXAMPLE III.

The temperature requirement and selectivity of a number of the catalysts shown in tables A and B for the preparation of a 430°C+ lubricating oil with a VI of 96 after de-waxing at -20°C, were intercompared in a hydrocracking test which was carried out under the following conditions.

#### 10 Feed:

Waxy heavy distillate lubricating oil fraction of a Middle East crude oil.

#### Properties of the feed:

15 VI after de-waxing at -20°C: 37  
Sulphur content: 3% by weight  
Nitrogen content: 1250 pbwm

#### Hydrocracking conditions:

hydrogen partial pressure: 140 bar  
space velocity: 1 kg. 1<sup>-1</sup>. hour<sup>-1</sup>  
hydrogen/feed ratio: 2000 N1. kg<sup>-1</sup>.

20

Catalyst bed: 250 ml

The catalysts were tested in the form of 1.5 mm extrudates.

The conditions relating to sulphiding and in-situ fluoriding of the catalysts and to de-waxing of the oils were the same as stated in example I.

25

In this test, an optimum catalyst should have a temperature requirement of at most 405°C and a selectivity of at least 51% by weight.

30

The results of this test are shown in table E.

TABLE E

Test cat. No.	Temperature requirement, °C	Selectivity, % by weight of feed
15	394	53
18	397	52
K	402	49
L	405	49
M	410	49
N	405	49

## EXAMPLE IV.

A number of the catalysts shown in tables A and B were employed in a hydrocracking test for the preparation of a 390°C<sup>+</sup> lubricating oil with a VI of 150 after de-waxing at -30°C.

Feed: bright stock slack wax

Properties of the feed:

oil content: 30% by weight  
sulphur content: 0.73% by weight  
nitrogen content: 86 pbwm

The hydrocracking was carried out under the following conditions, 70% by weight of the wax being converted;

hydrogen partial pressure: 130 bar  
space velocity: 1 kg . l<sup>-1</sup> . hour<sup>-1</sup>  
hydrogen/feed ratio: 1500 Nl . kg<sup>-1</sup>

Catalyst bed: 250 ml

The catalysts were tested in the form of 1.5 mm extrudates.

The conditions relating to sulphiding and in-situ fluoriding of the catalysts and to de-waxing of the oils were the same as stated for example I.

The results of this test are shown in table F.

Table F

Cat. tested, No.	Lubricating oil yield, % by weight
1	40
8	39
15	40
18	40
K	34
L	33
M	35

The results shown in tables C—F clearly demonstrate the superiority for the prepara-

tion of high viscosity index lubricating oils by hydrocracking, of catalysts according to the invention (catalysts 1—19) as compared with closely related catalysts outside the scope of the invention (catalysts A—G) as well as other catalysts previously proposed for the preparation of lubricating oils by hydrocracking (catalysts H—T).

## EXAMPLE V.

A number of the catalysts stated in table A were employed in the first stage of a two-stage process for the preparation of gasoline and middle distillate by hydrocracking a heavy hydrocarbon oil.

Feed:

Flash distillate of a Middle East crude oil.

Properties of the feed:

initial boiling point: 300°C  
final boiling point: 520°C  
28% by weight of the feed boils below 370°C

nitrogen content: 650 pbwm  
polyaromatic content: 60 mmol/100 g

Hydrocracking conditions:

temperature: 370°C  
pressure: 130 bar  
space velocity: 1.7 l . l<sup>-1</sup> . hour<sup>-1</sup>  
hydrogen/feed ratio: 1000 Nl . l<sup>-1</sup>

The catalysts were employed in sulphided form. Sulphiding of the catalysts was effected by contacting them for 16 hours with a mixture of hydrogen and hydrogen sulphide in a volume ratio of 7:1 at a temperature between 75 and 450°C and a pressure of 10 bar. In-situ fluoriding of the catalysts was carried out by supplying 2000 ppmw of fluorine in the form of fluorotoluene to the feed during the initial phase of the test until the required fluorine content of the catalyst had been reached. The catalysts were tested in the form of 1.5 mm extrudates.

The results of this test are shown in table G.

TABLE G

Cat. tested, No.	nitrogen content of the liquid product, pbwm	polyaromatic content of the liquid product, mmol./100g	portion of the liquid product boiling below 370°C, % by weight
2	4	4	43
3	12	5	41
4	4	3.5	43
5	4	2	43
6	7	4.5	41
7	13	6	42
12	4	2	43
13	4	2	43
A	60	10	39

The results stated in table G clearly demonstrate the superiority in the first step of a two-stage process for the preparation of gasoline and middle distillate by hydrocracking of catalysts according to the invention (catalysts 2—7, 12 and 13) as compared with a closely related catalyst outside the scope of the invention (catalyst A). The latter catalyst, which has too low a nickel and tungsten load and too low a compacted bulk density, removes less nitrogen and polyaromatics and produces less cracking than the catalysts according to the invention.

#### 15 WHAT WE CLAIM IS:—

1. A process for the conversion of hydrocarbons, wherein the hydrocarbons are contacted at elevated temperature and pressure and in the presence of hydrogen with a fluorine-containing nickel-tungsten catalyst having an alumina as carrier, which catalyst has a compacted bulk density (as defined hereinbefore) of at least 0.8 g/ml, comprises at least 3 parts by weight of nickel and at least 20 parts by weight of tungsten per 100 parts by weight of carrier, and is prepared as follows from an alumina hydrogel from which a xerogel having a compacted bulk density of less than 0.8 g/ml can be obtained by drying said hydrogel at 120°C. and calcining at 550°C.:

- 1) If the pore volume quotient (as defined hereinbefore) of the said xerogel is at least 0.5, the preparation of the catalyst is effected either
  - a) by drying and calcining the alumina hydrogel, incorporation of the metals and optionally fluorine into the xerogel,

and drying and calcining the composition, or

- b) by incorporation of the metals and optionally fluorine into the alumina hydrogel, and drying and calcining of the composition,
- 2) If the pore volume quotient of the said xerogel is less than 0.5, the preparation of the catalyst is effected by incorporation of the metals and at least part of the fluorine into the alumina hydrogel, and drying and calcining the composition, with the proviso that such a quantity of fluorine is incorporated that a xerogel with a pore volume quotient of at least 0.5 can be obtained by drying at 120°C and calcining at 550°C from the same alumina hydrogel when the same quantity of fluorine, but no metals, are incorporated therein.
2. A process as claimed in claim 1, wherein the catalyst is prepared via the xerogel route (as defined hereinbefore) and comprises 3—12 parts by weight of nickel and 20—75 parts by weight of tungsten per 100 parts by weight of alumina.
3. A process as claimed in claim 2, wherein the catalyst has a nickel/tungsten weight ratio between 1:5 and 1:7.
4. A process as claimed in any one of claims 1—3, wherein the catalyst is prepared via the xerogel route and comprises 0.5—20 parts by weight of fluorine per 100 parts by weight of alumina.
5. A process as claimed in any one of claims 1—4, wherein the catalyst is prepared via the xerogel route and least part of the fluorine is incorporated by in-situ fluoriding.
6. A process as claimed in claim 1, wherein

- the catalyst is prepared via the hydrogel route (as defined hereinbefore), in which the incorporation of the metals into the hydrogel is effected by treating the said hydrogel at a temperature between 60 and 250°C with an aqueous solution comprising a nickel compound and a tungsten compound.
7. A process as claimed in claim 1 or 6, wherein the catalyst is prepared via the hydrogel route and comprises 25—50 parts by weight of nickel and 50—80 parts by weight of tungsten per 100 parts by weight of alumina.
8. A process as claimed in claim 7, wherein the catalyst has a nickel/tungsten weight ratio between 1:1.5 and 1:5.
9. A process as claimed in claims 1 and 6—8, wherein the catalyst is prepared via the hydrogel route and comprises 10—30 parts by weight of fluorine per 100 parts by weight of alumina.
10. A process as claimed in claims 1 and 6—9, wherein the catalyst is prepared via the hydrogel route and at least part of the fluorine is incorporated while the alumina is still in the hydrogel form.
11. A process as claimed in any one of claims 1—10, wherein the catalyst is in sulphidic form.
12. A process as claimed in any one of claims 1—11, wherein lubricating oils are prepared by hydrocracking a mixture of heavy hydrocarbons.
13. A process as claimed in claim 12, wherein the catalyst employed is prepared via the xerogel route and comprises 0.5—10 parts by weight of fluorine per 100 parts by weight of alumina.
14. A process as claimed in claim 12, wherein the catalyst employed is prepared via the hydrogel route and comprises 10—25 parts by weight of fluorine per 100 parts by weight of alumina.
15. A process as claimed in any one of claims 12—14, wherein high viscosity index lubricating oils are prepared by hydrocracking a mixture of heavy hydrocarbons selected from: a) waxy lubricating oil fractions obtained in the distillation at reduced pressure of atmospheric distillation residues of waxy crude oils, b) waxes separated from these waxy lubricating oil fractions, c) waxes separated from lubricating oil fractions obtained by hydrocracking, and d) mixtures of two or more of the mixtures of heavy hydrocarbons mentioned under a, b and c.
16. A process as claimed in any one of claims 12—15, wherein high viscosity index lubricating oils are prepared by hydrocracking a mixture of heavy hydrocarbons at a temperature of 325—450°C, a pressure of 10—250 bar, a space velocity of 0.2—5.0 kg of feed per litre of catalyst per hour and a hydrogen/feed ratio of 100 to 5000 N1 of hydrogen per kg of feed.
17. A process as claimed in claim 16, wherein the process is carried out at a temperature of 350°—425°C, a pressure of 100—200 bar, a space velocity of 0.5—1.5 kg of feed per litre of catalyst per hour and a hydrogen/feed ratio of 500—2500 N1 of hydrogen per kg of feed.
18. A process as claimed in any one of claims 12—17, wherein high viscosity index lubricating oils are prepared by hydrocracking a mixture of heavy hydrocarbons, followed by hydrofinishing of the hydrocracked product.
19. A process as claimed in any one of claims 12—18, wherein high viscosity index lubricating oils are prepared by hydrocracking a mixture of heavy hydrocarbons, separation of the effluent of the hydrocracking reactor, or, if hydrofinishing is employed, separation of the effluent of the hydrofinishing reactor, by distillation into one or more light fractions and a residual fraction with an initial boiling point between 350 and 550°C, de-waxing of the residual fraction and recycling of at least some of the separated paraffins to the hydrocracking reactor.
20. A process as claimed in any one of claims 1—11, wherein light hydrocarbons are prepared by hydrocracking a mixture of heavy hydrocarbons.
21. A process as claimed in claim 20, wherein the catalyst employed is prepared via the xerogel route and comprises 10—20 parts by weight of fluorine per 100 parts by weight of alumina.
22. A process as claimed in claim 20, wherein the catalyst employed is prepared via the hydrogel route and comprises 20—30 parts by weight of fluorine per 100 parts by weight of alumina.
23. A process as claimed in claim 1 and substantially as hereinbefore described, with special reference to any one of the Examples.
24. Hydrocarbons obtained by the process claimed in any one of claims 1—23.
25. High viscosity index lubricating oils obtained by the process claimed in any one of claims 12—19.

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